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Performance Characteristics of Lithium-Ion Cells for Mars Sample Return Athena Rover

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ABSTRACT

In contrast to the primary batteries (lithium thionyl chloride) on the Sojourner Mars Rover and the upcoming 2001 Mars Rover, the Mars Sample Return (MSR) Athena Rover will utilize rechargeable lithium ion batteries, following the footsteps of MSP 2001 Lander. The MSR Athena Rover will contain a rechargeable lithium ion battery of 16 V and a total energy of 150 Wh. The mass and volume of the projected power system will be a maximum of 3 kg and 2 liters, respectively. Each battery consists of twelve cells (6-7 Ah), combined in three parallel strings of four cells (16 V) each, such that the capability of the Rover shall be maintained even in the event of one string failure. In addition to the usual requirements of high specific energy and energy density and long cycle life (100 cycles), the battery is required to operate at wide range of temperatures, especially at sub-zero temperatures down to -20^{0}C. In this paper, we report various performance characterization tests carried out on lithium ion cells, fabricated by different manufacturers under a NASA/DoD lithium ion battery consortium.

low-temperature peformance
storage

INTRODUCTION

Mission Objectives

NASA is undertaking a detailed exploration of the planet Mars in the form of several robotic spacecraft including Orbiters, Landers, Rovers and Microprobes. Following the recent successes of the Mars Pathfinder (Lander)/Sojourner (Rover) missions and on the heels of recent launches of Mars 98, similar Lander and Rover missions are being planned for each two years, starting from the year 2001. The Lander and Rover missions of 2003 and beyond are aimed at not only analyzing the Martian samples but also bringing them back to the Earth. The scientific goal of the MSR Lander/Athena Rover is broadly to determine the geologic and climatic history of a site in the ancient highlands of Mars with conditions supposedly favorable to the preservation of evidence of possible prebiotic or biotic processes. The objectives of these missions specifically include 1) taking color stereo images of the Martian surface, 2) determining the elemental and mineralogical compositions of Martian rocks and soil to derive information of their geology and climate, 3) obtaining microscopic images of the rocks and soils and 4) finding and collecting the samples most likely to preserve the evidence of ancient environmental conditions and possible life and storing them for return to Earth. Various payload elements in the MSR Athena Rover would thus include a Pancam for color stero imaging, an ∝- proton X-ray spectrometer for elemental composition analyses, Mossbauer, Mine-TES and Raman spectrometers for mineralogical composition analyses, a microscopic imager for close-up imaging and a mini-corer and sample container for sample collection and storage.

Power Subsystem for 03 Athena Rover

The main power source for the 2003 Athena Rover consists of a Ga-As solar cell array. The auxiliary power source augmenting the solar array for the nighttime and peak power operations is a rechargeable battery. Apart from the usual requirements of reduced mass and volume for the battery, there is greater emphasis on the low temperature performance for the Athena Rover mission. The batteries need to perform well down to -20°C, at moderate rates of charge and discharge. Combining this with their high specific energy of over 100 Wh/kg and energy density of over 200 Wh/l, lithium ion batteries emerge as the unique choice for these applications. Based on detailed testing of prototype cells from different manufacturers, lithium ion batteries have been chosen for the upcoming Athena Rover missions in 2003 and the subsequent follow on missions in 2005.

The lithium ion rechargeable battery for the 2003 Athena Rover will have 16 V and 150 Wh, with the total mass and volume of the battery not exceeding 3 kg and 2 liters, respectively. Three four-cells (each of 6-7Ah) strings will be connected in parallel with a diode protection, with one string providing some redundancy. Presently, the design of the battery is based on twelve cylindrical cells. However, alternate cell geometries, such as prismatic cells, could be a possibility. The above-specified energy of 150 Wh is to be made available after about two years of activation, though the preferred mode of storage during flight integration and cruise is still to be determined. The rechargeable battery shall be able to maintain the bus at a minimum of 11 Volts and not require the bus to exceed 18 Volts for recharge. One critical performance requirement for the battery is its ability to operate at sub-zero temperatures at moderate rates (maximum of C/2), without any reduction in the room temperature performance. The batteries will be provided with a heater to maintain temperatures of at least -20°C (minimum). Charging of the cells will be carried out at relatively higher temperatures (0 to +30°C). The battery will be charged with indigenously built charge control unit, which facilitates individual cell monitoring and cell balancing. A cycle life of over 200 cycles (to 80% of initial capacity) and two years of wet life are required for the mission.

NASA/DOD JOINT EFFORT FOR Li ION BATTERIES

There is a considerable commonality in the needs of NASA and the Air Force for advanced rechargeable lithium ion batteries, especially for LEO/GEO satellites. Accordingly, a NASA/DoD Inter-agency consortium was recently initiated with the main intent of developing domestic capability to manufacture lithium-ion cells and batteries with smart chargers for both NASA and Airforce needs.[1] Under this program, multiple manufacturers are being supported to provide the desired technological developments. As a part of this program, various lithium ion cells, in both prismatic and cylindrical configuration, and with capacities ranging from 4 to 40 Ah, are being evaluated at JPL under generic performance conditions as well as those relevant to Mars Surveyor Program 2001 Lander and MSR Athena Rover. In this paper, we report some of our recent observations on the behavior of Rover cells from these on-going tests. Similar tests carried out on larger cells (20-40Ah) for MSP 2001 Lander applications are being communicated in our companion paper.[2]

Li ION CELLS EVALUATION

The lithium ion cells evaluated contain proprietary electrolytes/electrode materials and designs to achieve the desired low temperature performance and/or cycle life. It was deemed essential to keep the manufacturers anonymous in this paper to promote parallel development at each of the respective organizations. All the cells have gone through a series of tests, aimed at establishing the baseline performance data of all the cells and validating lithium ion technology for the intended missions (Table 1). Accordingly, these tests consist of both generic and mission specific tests. The generic tests include cycle life at 100% DOD at ambient and low temperatures, and rate characterization at different rates (of charge and discharge) and temperatures . Mission specific tests include cycling at partial depths of discharge and at alternating high and low temperatures, and accelerated and real-time cruise and mission simulation tests. The miscellaneous tests are aimed at understanding the thermal characteristics, temperature-compensated voltage charging, safety and failure modes.

Li Ion Cells for MSR Athena Rover Applications

Physical, Conditioning cycles and EIS (impedance)

Generic performance	Mission specific	Miscellaneous
• Cycling at RT	• Cruise conditions	• V/T Charge
• Cycling at LT	• Cycling @ low DOD	• Thermal characteristics
• (Charge) rate vs. T	• Cycling at different temperature	• Storage Tests
• Discharge rate vs. T		
• Self discharge	• Mission simulation	• EIS vs. Cycling

Table 1. Description of tests being carried out on Li-ion cells for 2003 rover missions.

STATUS OF MSR ATHENA ROVER CELL TESTING

Cells from different sources, ranging in capacity from 4-7 Ah were tested for various tests listed in Table 1, after about five formation cycles under the voltage limits specified by the manufacturer.

Cycle Life at 25°C

Fig.1 displays the cycle life characteristics of various cells at 25°C. The cycling regime typically consists of a charge at C/5 to a charge cut-off voltage of 4.1, followed by tapered charging at the same voltage to C/50, or for an additional three hours, and a discharge at C/5 to 3.0 V, with a rest period of fifteen minutes between charge and discharge.

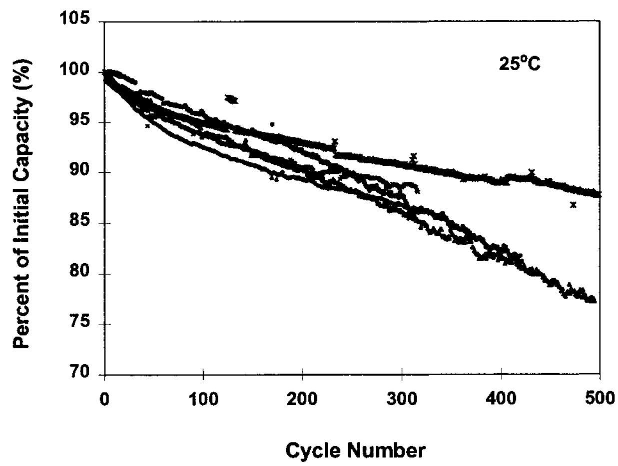

Fig. 1 Cycle life of Li ion cells (4-7 Ah) cells at 25°C for Mars Rover applications.

As may be seen from Fig. 1, the cycle life of the cells is generally acceptable from the mission point of view, with over 90% of the initial capacity being retained over 200 cycles. There is also noticeable spread in the capacity fade rate in the above cells from different manufacturers, stemming partly from the electrolytes (low temperature), the electrode materials and partly from the design parameters.

During the cycling, the C/D ratio remains the same, at a value slightly higher than unity. However, both the open circuit voltages at the end of charge and discharge show noticeable change as shown for one cell in Fig.2. The decreases in the open circuit voltage after charge as well as the increase after discharge reflect the increasing cell impedance during cycling.

The larger increase in the OCV after discharge, compared to the decrease after charge, is not due to a slower discharge kinetics (the charge kinetics is relatively slower as discussed in the following sections) but is due to the shape of the OCV vs. SOC curve which is more sloping at lower states of charge. The decrease in the open circuit voltage (15 minutes after) after charge as well as the increase after discharge reflects the increasing cell impedance during cycling.

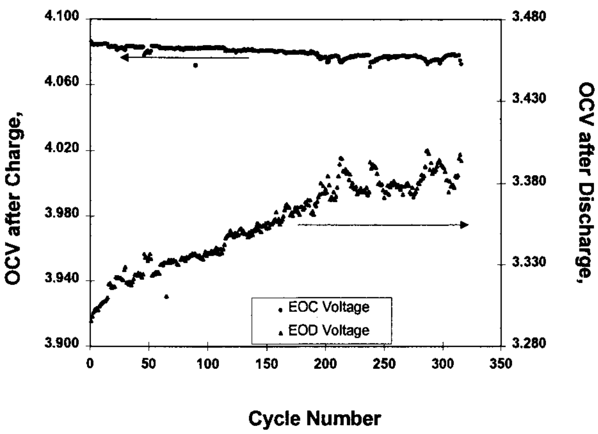

Fig. 2: OCV after charge and discharge during cycling of Li ion cells (4-7 Ah) cells at 25°C.

Cycle Life at -20°C

The MSP 2003 Athena Rover requires the Li ion cells to perform well at –20°C. Accordingly, we cycled the cells at –20°c, with both the charge and discharge performed at low temperature.

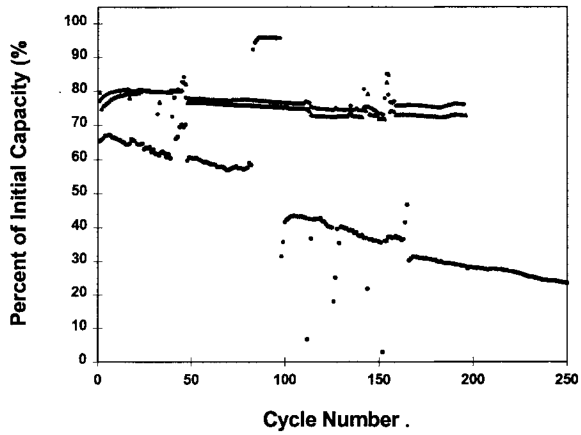

Fig. 3: Cycling of Li ion cells (4-7 Ah) cells at -20°C for Mars Rover applications.

In the real case, however, the charge would be at a higher temperature, around 0°C, which is easier on the cell in terms of charge acceptance. Charging is typically carried out at C/10 to 4.1, with an additional three hours of tapered charge at this voltage and the discharge is performed at C/5 to 3.0 V.

As shown in Fig. 3, the initial capacity at –20°C is a good 70-80% of the room temperature capacity, which is quite impressive. Similar improvements have been made JPL[3] and elesewhere[4] relative to develop low temperature electrolytes for Li ion batteries. The capacity fade rate during cycling at the low temperature is also fairly impressive, at least in one case. However, in one set of samples, we have observed an unusually rapid capacity fade, which may partly be attributed to the failure of the test chamber resulting in a higher cell temperatures of ~25°C. From this, and from various other tests, we have noticed that the low temperature performance is very sensitive to any prior exposure of the cell to higher temperatures. The rapid buildup of the surface film or solid electrolyte interphase (SEI) on the graphite anode during ambient or high temperature cycling may be responsible for the subsequently poor low temperature performance. We have therefore been carrying a variable temperature cycling test on various Li ion cells to assess and analyze this.

A comparison of the OCV's after charge and discharge during cycling at room temperature and –20°C is shown in Fig. 4.

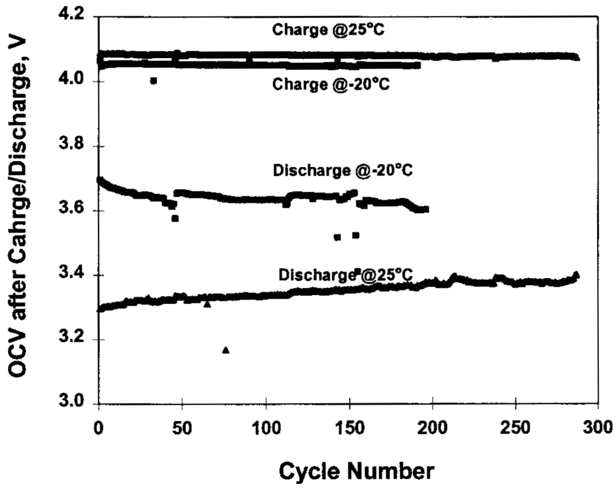

Fig. 4: Comparison of the OCVs after charge and discharge during cycling at 25°C and –20°C.

It is clear from Fig. 4 that the OCV after charge is lower (and after discharge is higher) during cycling at low temperature, compared to the cycling at ambient temperature. This illustrates the relatively poor kinetics of charge and discharge at low temperatures.

Characterization : Different Rates and Temperatures

The cells were examined for their rate capability during discharge as well as charge at different temperatures. Discharge and charge rates of C/10, C/5, C/2 and C were used both for charge and discharge, with the discharge tests preceded by charge under standard conditions C/10) and vice versa. The temperature range included –20 to + 40°C, in steps of 20°C. These studies are mainly to assess the applicability of these cells for the MSR Athena Rover applications. Fig. 6 shows the variation of discharge capacity of Li ion cells from one manufacturer as a function of rate and temperature.

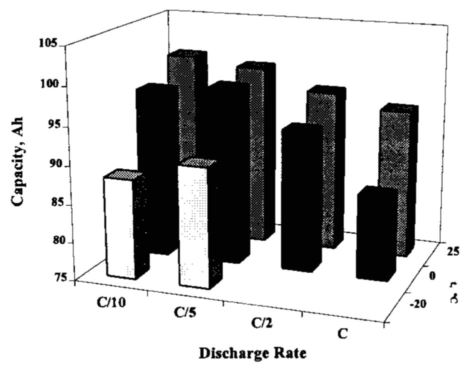

Fig. 5 : Discharge capacity as a function of rate and temperature of Li ion cell for Mars Rover.

As shown in figure 5, Li ion cells can provide high proportion (over 80% of RT capacity) at –20°C at moderate rates of C/5, a critical requirement for the Rover mission. It should be realized that these high yields at low temperature are possible, even though the preceding charges were carried out at the low temperatures as well. Fig. 5 summarizes the performance of the cells at various rates and temperatures in the form of Ragone plots.

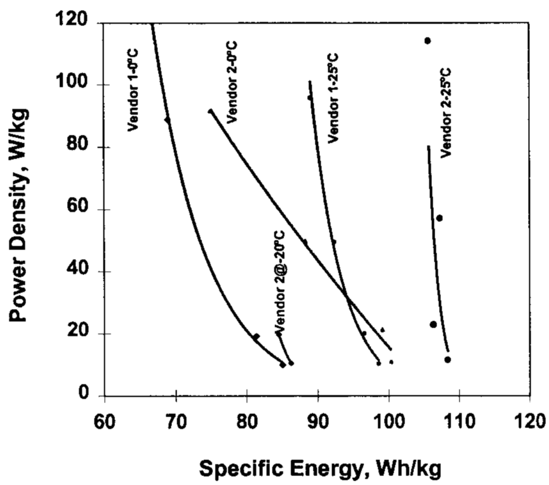

Fig. 6 : Ragone plots at various temperatures of Li ion cells for MSR Athena Rover applications

The cells have shown impressive specific energies of 90-100 Wh/kg even at high power densities of 100 W/kg. The corresponding values at 0°C are around 80 Wh/kg.

EIS during cycling

It is implied from the observed OCV's after charge and discharge during cycling (Fig. 4) that the cell impedance increases during cycling. To get a quantitative idea of this impedance buildup, ac impedance measurements were made after each 100 cycles. Fig. 6 shows the typical EIS (Electrochemical Impedance Spectroscopy) plots during cycling.

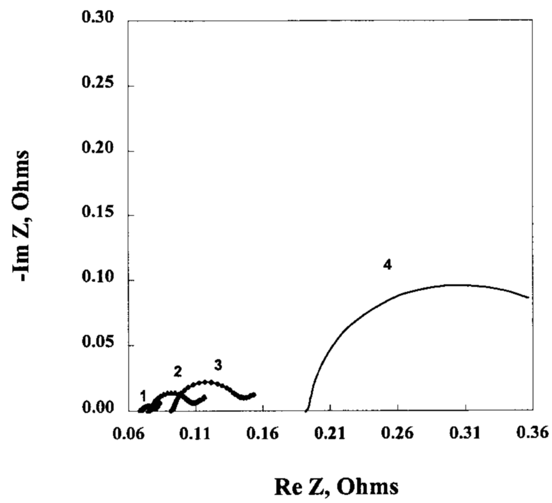

Fig. 6 EIS plots of Li ion cells after 1) 5, 2) 100, 3) 200 and 4) 300 cycles at 25°C

The impedance of the Li ion cell increases appreciably during cycling. There is an increase in the series (Ohmic) resistance as well as in the relaxation loop. From the half-cell studies, it appears that the relaxation loop is primarily related to the surface film (SEI) on the graphite anode. There is thus a continued buildup of the SEI during cycling, which impedes the kinetics of lithium intercalation/deintercalation at the anode.

Storageability of Li ion cells

The missions to Mars have typical cruise times of 7-12 months. This combined with pre-cruise storage requires the batteries to be dormant for a maximum of 2 years before their first use. The expected mode of storage is in the open circuit mode at a storage temperature yet to be determined. We have carried out a series of storage tests at various states of charge and storage temperatures for a storage period of eight weeks, to help identify the optimum storage conditions. Fig. 7 shows the storage characteristics of one set of samples.

The cells sustained some reversible loss, equivalent to self-discharge, and some permanent loss in the capacity. The latter is obviously a concern to the project. The permanent capacity loss is typically 3% and 14% at 50% and 100% state of charge, respectively at 40°C. The corresponding values at 0°C are, however, considerably less and are 0% and 3 %, respectively.

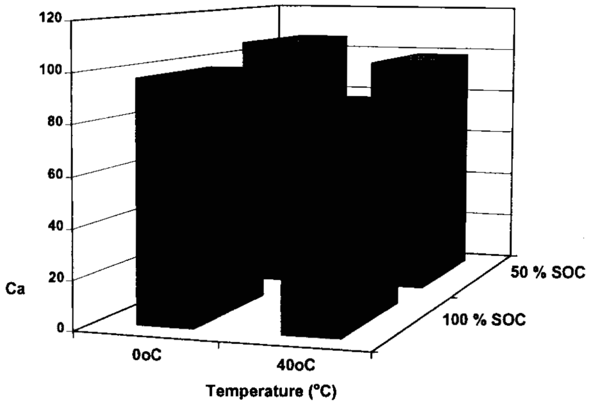

Fig. 7 Capacity (in the second cycle) of Li ion cells after storage for eight weeks

Charge voltage vs. temperature

The Li ion system has a negative temperature coefficient in the OCV, similar to the nickel system. In addition to this thermodynamic effect, the kinetics of Li intercalation and deintercalation are slowed at low temperatures, partly due to the increased Ohmic polarization in the electrolyte. Higher charge cut-off voltages should be feasible, without facilitating the Li plating process on the anode and/or deep delithiation at the Li_xCoO_2 cathode, as shown in Fig. 8.

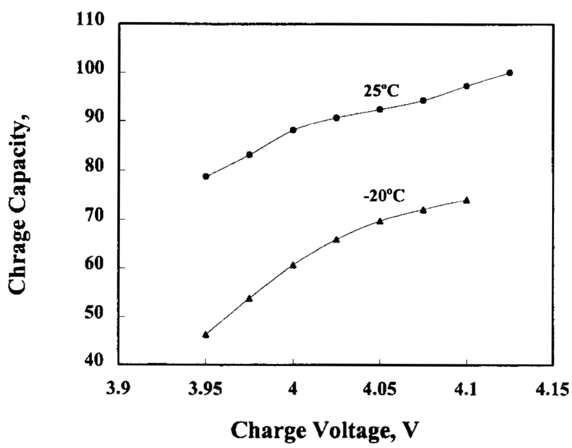

Fig. 8 Charge capacity vs. charge cut-off voltage in Li ion cell at different temperatures

To determine the effect of charge potential on capacity, these experiments were done both by changing the charge cut-off voltage in steps of 20 mV in a single charge and also by performing two charge/discharge cycles at each charge voltage. As may be seen from the figure, at low temperatures, higher charge voltages need to be applied to enable complete (to the name plate capacity) charging of the cell. These studies will have to be corroborated by half-cell studies to ensure that the anode potentials will not approach Li plating potentials at these higher charge voltages.

ACKNOWLEDGEMENT

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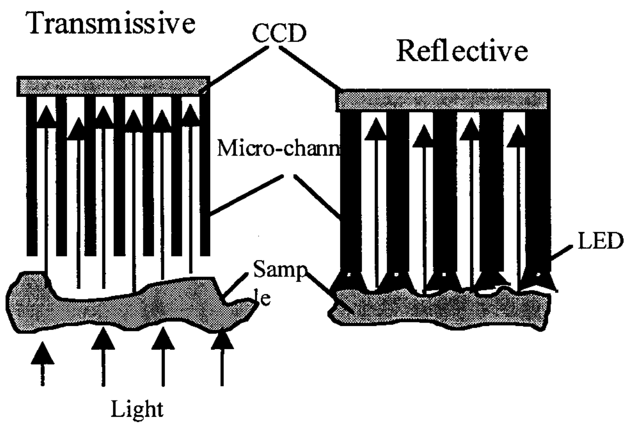
4) For example, Ein-Eli, Y., *et al*, *J. Electrochem. Soc.*, **1996,** 142, L273.

A technology breakthrough invented at JPL. Can be built as either transmissive or reflective microscopes.

A lightweight, lower power, no focus adjustment microscope is desirable for Mars in-situ program and HEDS.

Using a micro-channel plate to generate an one-to-one mapping from sample to the pixels of a CCD or APS sensor. Only the light parallel to the channel walls can reach the pixels, while light in other directions will be absorbed by the walls.



Traditional microscope is heavy, in kilograms. And the focus adjustment is time consuming.

The microscope-on-chip is:
***Lightweight (<50g)**
***Low power (<0.1-w)**
***No lens**
***No moving parts**
***High resolution (up to 2μ).**

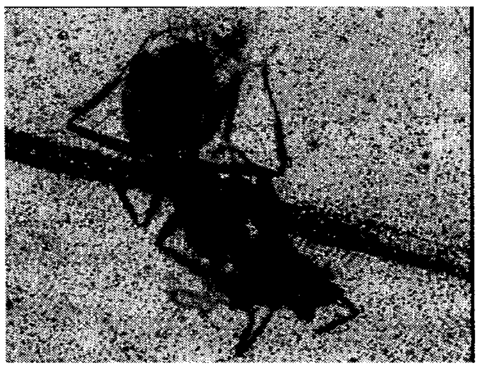


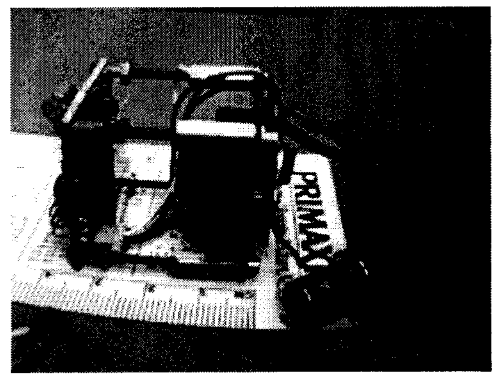
Image of an ant taken by the first prototype of microscope-on-chip.

Accomplishments

1. Performed theoretical modeling
2. Fabricate the first prototype microscope.
3. Designed reflective microscope.

Next step:

Fabricate reflective microscope-on-chip.



Prototype of transmissive microscope-on-chip, fund by DRDF and UPN632